

### Isomerization of terpenoid hydrocarbons by acid-washed alumina

Numerous reports have appeared<sup>1</sup> on the structural alteration of organic compounds during column chromatography on alumina or silicic acid. However, the properties of "acid-washed alumina" in this regard have not been investigated. The present

<sup>1</sup> E. LEDERER AND M. LEDERER, *Chromatography*, 2nd Ed., Elsevier Publ. Co., Amsterdam, 1957, p. 61 *et seq.*

\* Mention of a specific commercial product does not constitute endorsement by the United States Department of Agriculture.

report concerns the isomerization of two terpenoid hydrocarbons, squalene and neophytadiene, during chromatography on this adsorbent.

Squalene (Eastman-Kodak\*) was purified by fractional distillation, and the purified material was chromatographed (5 g) on a column (1.25 in.  $\times$  4.5 in.) of Merck acid-washed alumina (activated at 160° for 15 h). The column was washed with petroleum ether which completely eluted the terpene in seven successive fractions of 100 ml each. The infrared spectra of the seven fractions were identical: the broad band at 11.7–12.4  $\mu$  ( $R_1R_2C=CHR_3$ ) of squalene had disappeared, a moderate band at 11.25  $\mu$  ( $R_1R_2C=CH_2$ ) had appeared and the absorption at 6.01  $\mu$  ( $R_1R_2C=CHR_3$ ) of squalene had shifted to 6.07  $\mu$  ( $R_1R_2C=CH_2$ ). These spectral shifts and the presence of a slight inflection at 234  $m\mu^2$  were suggestive of a squalene  $\rightarrow$  regenerated squalene<sup>3</sup> isomerization during chromatography. However, minor infrared spectral differences were observed between the eluted material and regenerated squalene: the former showed weaker, less distinct bands in the 8.5–10.2  $\mu$  region, a slight inflection at 7.35  $\mu$  (isopropyl-) and no adsorption at 11.7–12.4  $\mu$ . Thus, the possible presence of isomers other than regenerated squalene in the eluted material was indicated.

Isomerization of neophytadiene<sup>4–6</sup> (3-methylene-7,11,15-trimethyl-1-hexadecene) also occurred under the above conditions. The infrared spectrum of the eluted material showed an intense band at 10.38  $\mu$  (*trans*—CH=CH—) in place of the 10.1, 11.1 and 11.2  $\mu$  bands ( $R_1R_2C=CH_2$  and  $RCH=CH_2$ ) of neophytadiene; these characteristics are similar to the spectra reported<sup>4,7</sup> for Phytadiene C and Phytadiene Fraction V.

In studies on the isolation of natural products, the possibility of isomerization of terpenes during chromatography on acid-washed alumina should be recognized. Perhaps the reported presence<sup>2,8</sup> of regenerated squalene in cigarette smoke condensates was the result of such isomerization.

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<sup>4</sup> R. L. ROWLAND, *J. Am. Chem. Soc.*, 79 (1957) 5007.

<sup>5</sup> R. N. GLADDING, W. B. WARTMAN, JR. AND H. E. WRIGHT, JR., *J. Org. Chem.*, 24 (1959) 1358.

<sup>6</sup> I. ONISHI, M. NAGASAWA, H. TOMITA AND T. FUKUZUMI, *Bull. Agr. Chem. Soc. Japan*, 22 (1958) 57.

<sup>7</sup> A. RODGMAN, *J. Org. Chem.*, 24 (1959) 1916.

<sup>8</sup> A. I. KOSAK AND J. S. SWINEHART, *Chem. and Ind. (London)*, (1958) 1007.

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